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Published in:
Sustainable Energy & Fuels

Link to article, DOI:
[10.1039/C7SE00073A](https://doi.org/10.1039/C7SE00073A)

Publication date:
2017

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Cui, M., Nie, H., Zhang, T., Lovley, D. R., & Russell, T. P. (2017). Three-dimensional Hierarchical Metal oxide-Carbon Electrode Material for High Efficient Microbial Electrosynthesis. *Sustainable Energy & Fuels*, 1, 1171-1176. <https://doi.org/10.1039/C7SE00073A>

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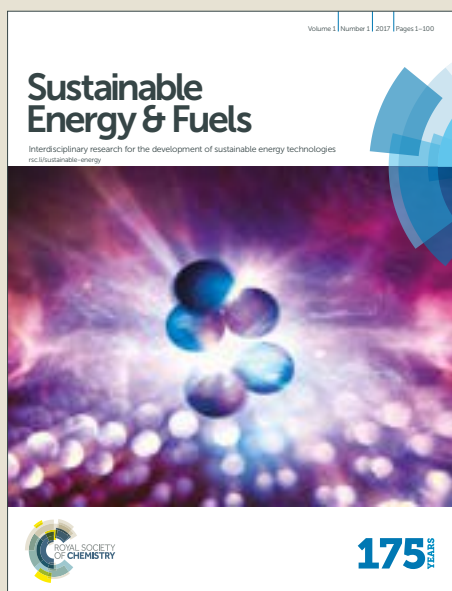
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Sustainable Energy & Fuels

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The production of hierarchical hybrid conductive materials that are mesoporous, with pores spanning from sub-micron to microns in size, is important for large-area electrode applications. Here, a simple one-step, low-cost method to fabricate a metal oxide-carbon hybrid materials with a hierarchical pore structure in a microwave oven is demonstrated. Microwave pyrolysis of ferrocene using carbon felt as a microwave absorber, a method that is rapid (tens of seconds), does not require harsh conditions nor costly equipment is utilized, and can be readily scaled up. The produced material has a high specific surface area, a multi-length scale porous structure and a high conductivity, and is quite stable, making it promising for many practical applications. As an electrode in microbial electrosynthesis, the performance is improved by a factor of five and an optimal biofilm of the microorganism is formed on the surface.

Introduction

Since the Industrial Revolution, the wide usage of fossil fuels and human activities have upset the original balance of the carbon cycle, leading to climate change, energy source diminishment, air pollution, and water pollution, just a few of the resultant problem that threaten our existence.¹ Since natural photosynthesis alone cannot convert all the carbon dioxide (CO₂) emitted by fossil fuel combustion to usable organic compounds, a new technology of CO₂ conversion to restore the carbon balance on the Earth is needed. One option is microbial electrosynthesis (MES), a microorganism-catalyzed reduction of CO₂, where electric energy is captured in organic molecules generating products that are readily stored and easily distributed.^{2,3} The combination of MES with solar cells, devices that convert light into electricity, represents an artificial form of photosynthesis that has many potential advantages over bioenergy strategies that rely only on biological photosynthesis.² Solar cells have seen dramatic improvement in efficiencies with multijunction solar cells

having efficiencies of ~46%.⁴ The concept of MES, however, has only recently been demonstrated by *Nevin et al.* with a biocathode-driven reduction of CO₂ to acetate.^{2,3,5}

The large-scale practical application of MES requires improved MES efficiency. The species of microorganism, the working environment (chamber design and feeding condition), and the electrode material are all important factors that influence the efficiency of an MES cell.⁶⁻¹⁰ Same as in other energy storage devices and electrochemical systems, the performance of electrode in the microbial electrochemical (ME) cells plays a crucial aspect in efforts to enhance the performance of ME cells. A desirable electrode in ME cells acts as not only the electron transfer conductor, but also a substrate on which cells adhere, and a diffusion pathway to accommodate the culture media throughout the electrode structure. However, only a few reports on new cathode material development and surface modification strategy have appeared.⁷⁻¹⁰ Performance improvement has been achieved by incorporating positively charged functional groups to enhance electrode-microbe electron transfer¹⁰ using nanoparticles or nanowires to reduce the activation energy of electron transfer,⁹ or growing carbon nanotube (CNT) on structural materials.^{7,9} Among these, reticulated vitreous carbon modified with CNTs has shown the most promise for increasing MES performance with the highest reported current density and productivity of organic molecules. As an alternative to modifying the scaffold material with CNT, a direct growth of graphitized carbon substructure on a carbon-based material reduces the complexity, difficulty and cost of CNTs synthesis¹¹⁻¹³, thus potentially leading to more economically viable electrode materials.

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Electronic Supplementary Information (ESI) available, see DOI: 10.1039/x0xx00000x

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Except for selecting proper materials, one also needs to construct an appropriate architecture of electrode to better align with the MES process. A three-dimensional (3D) carbon-based porous framework is an ideal structure for MES electrodes, due to the enhanced electron transfer, increased microorganism density based on surface to volume ratio, and improved mechanical stability.^{6, 14–22} Recently, 3D porous electrode has attracted attention in enhancing the overall performance of energy storage device due to the synergistic advantages of multilevel morphologies. However, common fabrication methods of 3D porous electrodes involve with tedious adsorption coating on scaffold template^{23,24}, physical mixing process^{25,26}, atomic layer deposition under gas protection^{27,28} and other composite in-situ growth route²⁹. Therefore, most of the fabrication processes of these electrodes were time-consuming, insufficient and expensive.¹⁷ Developing a simple preparation method of highly effective electrode remains crucial and challenging.

Herein, we report a simple one-step, low-cost method to grow Fe(III) oxide-graphitized carbon nanostructures directly on carbon felt, building a 3D hierarchical material for microbial electrosynthesis. An acetate productivity of more than 2.48×10^5 mM day⁻¹ m⁻³, together with an electron recovery rate of 86 ± 9 % (in acetate), was achieved with such an electrode, while native carbon felt cathode only led to a rate of acetate production of $\sim 5.19 \times 10^4$ mM day⁻¹ m⁻³ with an electron recovery rate of 73 ± 7 % (in acetate). Optimal biofilm formation, a crucial component in microbial electrosynthesis, was also achieved throughout the hierarchical electrode, even within the interior of the carbon felt.

Experimental Section

Materials

Ferrocene and hexane were purchased from Sigma Aldrich. Carbon felt was purchased from Alfa Aesar. All chemicals were used without further purification. *Sporomusa ovata* (DSM 2662) was obtained from Deutsche Sammlung Mikroorganismen und Zellkulturen and routinely grown in DSM medium 311 (omitting betaine, fructose, casitone, and resazurin) with hydrogen as the electron donor (H₂-CO₂ [80:20]) at 30 °C under strict anaerobic conditions as previously described.^{2,3}

Electrode preparation

Carbon felt with the thickness of 10 mm were cut into blocks of 80mm×30 mm. They were dipped into saturated solution of ferrocene in hexane and then taken out. After the fast evaporation of hexane by air gun in the fume hood, the carbon felt electrodes were put in a microwave oven (GE Appliance, 1000Wt) and irradiated at 2.45 GHz for 40 seconds. Subsequently, we dipped the carbon felt electrodes in the saturated ferrocene solution again, and then repeated the microwave pyrolysis process for another 3 times.

Characterization

The morphology was studied with FESEM (FEI Magellon 400, Japan) and high-resolution transmission electron microscopy (JEM-2000FX, JEOL, Japan). X-ray diffraction (XRD) experiments were performed in a Shimadzu XRD-6000 X-ray powder diffractometer with Cu K (λ=0.154 nm) radiation at a generator voltage of 45 kV and a current of 40 mA. X-ray photoelectron spectra (XPS) were obtained on a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. Depth profiling was done by collecting spectra at 15° and 75° take-off angles with respect to the plane of the sample surface. The analysis at 15° corresponds to compositions with a penetration depth of ~10 Å and the one at 75° corresponds to compositions with a penetration depth of ~40 Å.

Microbial electrosynthesis

Unmodified carbon felt cathode (80mm×30mm×10 mm) and the achieved 3D cathode (modified from the carbon felt cathode with above mentioned size) were tested at 25 °C in a three-electrode, dual-chambered system, with *Sporomusa* grown in the cathode chamber as previously described.^{2,3} The tested cathode and graphite stick anode (65 cm²; Mersen, Greenville, MI) were suspended in 250 ml of media in two chambers which are separated by a Nafion 117 cation-exchange membrane (Electrolytica, Amherst, NY). The anode chamber was continually bubbled with N₂-CO₂ (80:20). The cathode was poised with a potentiostat (ECM8, Gamry Instruments, PA, USA) at -900 mV (versus Ag/AgCl). Hydrogen-grown cultures of *Sporomusa* were established in the cathode chamber in a medium that described above, and hydrogen containing gas mix N₂-CO₂-H₂ (83:10:7) was used as additional electron donor to gas out the cathode chamber for biofilm growth. The cathode gas mix was switched to N₂-CO₂ (80:20) after several fresh medium swaps. Acetate was measured via high performance liquid chromatography (HPLC) as previously described.³

Results and Discussions

Carbon felt was chosen as the base material here due to its high conductivity, high surface to volume ratio, and excellent chemical and physical stability.^{30,31} The 3D hierarchical metal oxide-carbon material was fabricated by microwave pyrolysis of ferrocene deposited on carbon felt. The high microwave absorption capability of carbon felt, due to its relative permittivity and porous structure which results in a high permeability of microwaves, increased the temperature of the entire volume to 1000 °C uniformly and efficiently.^{17, 32} Ferrocene was decomposed and formed nanostructures on carbon felt in a few seconds.^{33,34} As shown in the schematic illustration, the carbon felt was immersed in a saturated ferrocene solution in hexane. After drying, the pre-treated carbon felt was pyrolyzed under microwave irradiation at 2.45 GHz for 30 s. This immersion and irradiation process was repeated three times to fully grow the substructures on the carbon felt.

The morphology of the original carbon fiber and the resultant structure after microwave irradiation was investigated by scanning electron microscopy (SEM). The average diameter of the original carbon fiber is $\sim 14\ \mu\text{m}$ (**Figure 1A**) with a relatively smooth surface. After microwave heating, closely packed nanostructures grew directly on the carbon fibers, resulting in a rough shrub-like surface with an increase in the average diameter of the fibers to $\sim 22\ \mu\text{m}$ (**Figure 1B**). A hierarchical structure, consisting of micron-sized pores ranging from 20–100 μm and nano-scale pores, hundreds of nanometers in size, was formed (**Figure 1C,D**). This topology allowed microorganism to infiltrate into the interior of

electrode and provided more active electron transfer locations.

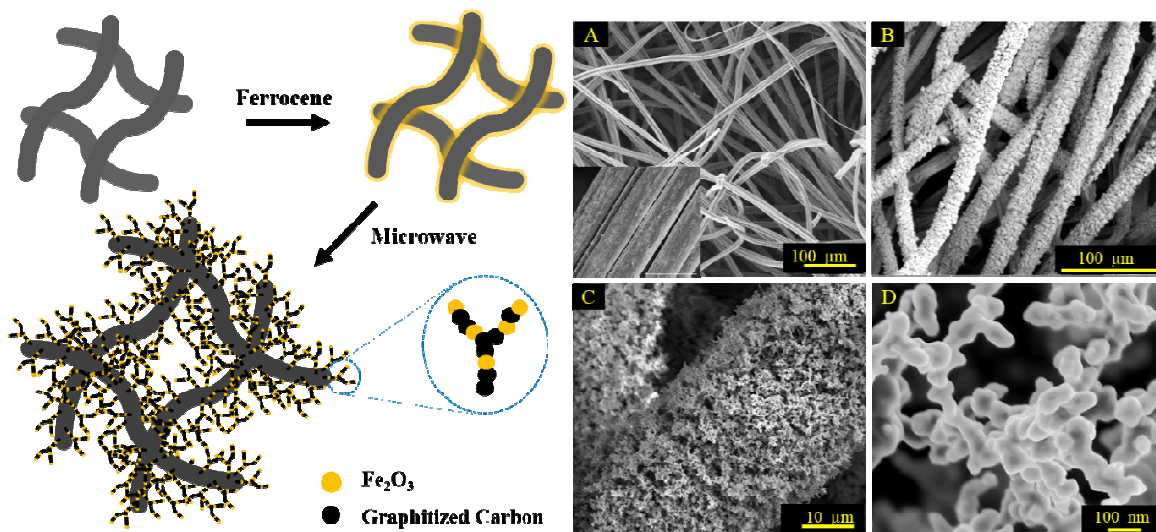


Figure 1. Schematic for the formation of hierarchical metal oxide-carbon structure (Left). SEM images of carbon felts (Right): (A) SEM image of untreated carbon fibers, and insert is the high magnification image; (B) SEM image of carbon fibers with the deposition of the hybrid layer of carbon and iron oxide; (C-D) Low- and high-magnified SEM images of the pyrolysis products on carbon fibers, and both SEM images of modified carbon felt illustrate the nano-dendritic structure.

To determine the exact composition of the dendritic nanostructures, the samples were characterized by X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRD). XPS of microwave irradiated carbon felt clearly showed peaks corresponding to Fe, C and O, while no Fe was observed for the untreated carbon-felt starting material. Further, the associated satellite peak at 719 eV appeared between the two peaks at 725 eV and 711 eV, which can be assigned to Fe 2p_{1/2} and Fe 2p_{3/2}, respectively, confirmed the presence of Fe₂O₃ in the nanostructures (**Figure 2A, 2B**).^{35, 36} The peaks at 29.6° and 47.6° in the XRD pattern are associated with the (002) and (101) planes of the graphitized carbon (**Figure 2C**)³⁷ and the lamellar sub-structures in the transmission electron microscopy (TEM) image confirm the formation of graphitized carbon (**Figure 2D**). The new appearing reflections seen from 30–40° and in the higher angular region arise from Fe₂O₃, agreeing well with the XPS results. Overall, the co-existence of graphitized carbon and Fe₂O₃ in the dendritic nanostructures is confirmed by XPS, XRD and TEM. The hybrid property of nano-dendritic materials was further identified by the contrast difference in TEM image (**Figure S1**).

We postulate a reaction mechanism for the co-formation of graphitized carbon and Fe₂O₃. Under microwave irradiation, the carbon fibers were rapidly heated to thousands of degrees, far beyond the thermal decomposition temperature of ferrocene. Thus, the ferrocene coated on the carbon fibers decomposed into iron particles and carbonaceous material.^{38–40} The iron particles catalyzed the carbonization of cyclopentadienyls and yielded graphitized carbon, as well as more iron particles. These products served as new microwave absorbers and further decomposed the ferrocenes to produce more graphitized carbon and iron particles. Therefore, by varying the amount of ferrocene coated onto the fiber and exposure to the microwave, the degree of surface modification degree of the carbon felt can be controlled.

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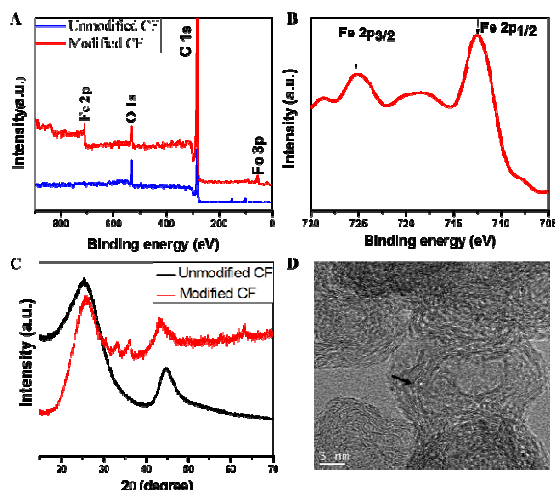


Figure 2. (A, B) XPS analysis of treated carbon felt proves the nano-dendritic structures consist of Fe_2O_3 and graphitized carbon. (C) X-ray diffraction pattern of the deposited hybrid layer of pyrolysis product further demonstrates the presence of Fe_2O_3 and graphitized carbon. (D) TEM image illustrates the lamellar structure of graphitized carbon.

The chemical and structural stability are important for the actual use of the electrode materials. The presence of Fe_2O_3 nanoparticles with the carbon material may also lead to better electron transfer, because of the semi-conductive properties of Fe(III) oxides in microbial extracellular electron transfer.^{41,42} It is also important to note that the iron oxide-graphitized carbon is quite stable, with no obvious morphological change, as evidenced by scanning electron microscopy (SEM), after sonicating the electrode in water for 30 mins (Figure S2). Additionally, the high pH value in the cathode chamber (pH ~ 7.2 medium) should make the dissolution of iron oxide into the solution neglected. The following discussion on the long-term high output of acetate also supports the stability of such iron oxide-carbon materials.

As an electrode in an MES cell, the 3D Iron oxide-graphitized carbon felt has the following advantages: (1) large specific surface area arising from the deposited nanostructure; (2) more adherent points for the microorganism; and (3) hierarchically porous structures arising from inter-fiber and inter-nanostructure enhances culture media transport and cell penetration. (4) Improvement in microbial extracellular electron transfer mediated by semi-conductive metal oxide nanocolloids.^{41,42}

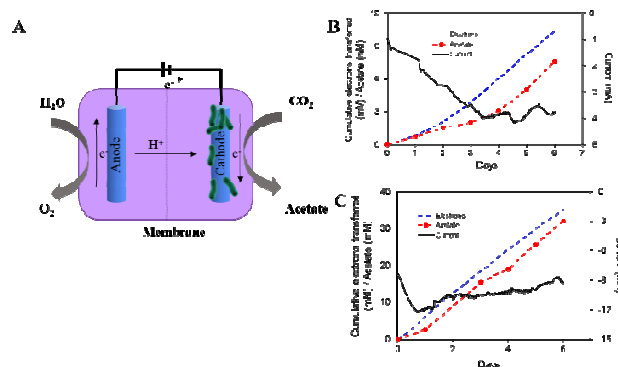
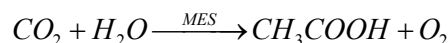


Figure 3. Schematic of the apparatus for microbial electrosynthesis (A). Measurements of electron consumption, acetate and current production over time with different cathodes: untreated carbon felt cathode (B) and modified carbon felt (C)

An H-cell device comprising an anode cell, a cathode cell, and a separating membrane was used for microbial electrosynthesis. The microorganism on the cathode extracted the electrons from the electrode and reduced CO_2 to acetate (Figure 3A).^{2,3} The overall net chemical reaction is



As shown in Figure 3, by using the modified electrode, the efficiency of electrosynthesis increased greatly, in comparison to the unmodified carbon felt. An efficiency of $2.48 \times 10^5 \text{ mM day}^{-1} \text{ m}^{-3}$ for acetate production with $86 \pm 9 \%$ of the electrons recovered in acetate was achieved using this electrode (Figure 3B). When carbon felt was used as the cathode, the rate of acetate production is $\sim 5.19 \times 10^4 \text{ mM day}^{-1} \text{ m}^{-3}$ with a recovery of $73 \pm 7 \%$ of the electrons in acetate (Figure 3C). The production of acetate relative to the volume of the electrode was used as a new evaluation criterion, as the volume of electrode is a more precise measure of the size of the reactor for engineering applications, as opposed to the surface area. In comparison, the modified, hierarchical electrode with the dendritic hybrid metal oxide-carbon nanostructure showed a five-fold increase in acetate production over the carbon felt, further underscoring the efficiency of this electrode geometry for microbial electrosynthesis. As shown in Figure S3B, efficient acetate production was maintained with these electrodes for more than 40 days, demonstrating the functional stability of the modified electrode.

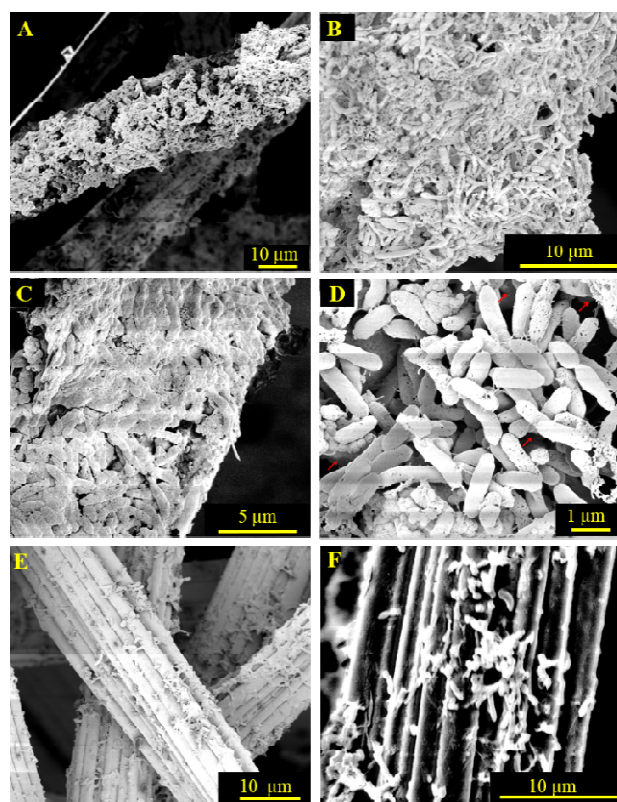


Figure 4. (A-B) SEM micrographs of microorganism films on 3D hierarchical electrode surface at different magnification. (C) SEM image of microorganism on the electrode interior. (D) SEM image of microorganism on the surface of nanostructured hybrid layer at high magnification. (E-F) SEM images of microorganism films on plain carbon fiber at different magnification.

As expected, when the hierarchical electrode was used in MES, where the acetogenic bacteria *Sporomusa ovata* was the microorganism, a mature biofilm was formed on the electrode that wrapped around carbon fiber. As shown in **Figure 4A-4D**, coherent microorganisms attached to the surface and adhered to each other. Even for the internal fibers, a densely packed biofilm was found on the surface (**Figure 4C, 4D**). Optimal wetting ability of modified carbon felt favors culture media transport and cell penetration. At a higher magnification (**Figure 4D**), it appeared that more than a single layer of biofilm was formed on the deposited layer, as evidenced by the surface roughness. These results demonstrated that the multilevel porous structure of 3D electrode allowed sufficient culture media exchange to support internal microorganism biofilm growth. As a control, **Figure 4E, 4F** showed that only a few microorganisms attached to the plain carbon fiber, which further suggested that the 3D electrodes with the nanostructured hybrid surface and multi-length scale porosity provided a superior environment for microbial colonizing.

Conclusion

In summary, we have developed a functional 3D hierarchically porous electrode by *in-situ* microwave pyrolysis of ferrocene on carbon felt. This electrode is an attractive target for microbial electrosynthesis: high conductivity, increased surface area, interconnected macroporosity, improved electrochemistry and robust mechanical support. The unique character of this 3D electrode provided sufficient space for microbial colonization, culture media transport and improved electro-activity. For the microbial reduction of carbon dioxide by *Sporomusa ovata*, a five-fold increase in acetate production rate was achieved with these 3D electrodes in comparison to carbon felt. This simple, rapid and low-cost pyrolysis method can be extended to fabricate other nanostructured architectures for more energy storage devices and electrochemical systems.

Acknowledgements

M. Cui and H. Nie contributed equally to this work. The modification of the electrode surface using the hybrid materials was supported by the US Department of Energy, Office of Basic Energy Sciences under contract DE-FG02-96ER45612. The microbial electrosynthesis and the characterization of the device performance was supported by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy [DE-AR0000159].

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